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E-beam and RIE examination of chemically amplified positive-tone resist CAMP6

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Abstract

We report on e-beam lithographic (EBL) and reactive ion etching (RIE) experiments with the positive chemically amplified resist (CAR) CAMP6 used for the fabrication of silicon structures ranging in size from the nanometer scale up to the micron scale in relatively thick resist film. Direct-write EBL at 30 keV was used to study the pre- and post-exposure processing on the resulting resist-relief structures. We measured the basic resist characteristics and also the influence of proximity effects. The resolved single-layer resist-relief structures at optimised process conditions have shown high aspect ratios with nearly vertical side-walls and T-top profiles in 0.6–1.7 μm thick films up to nanometer lateral dimensions. The paper will discuss the deep pattern transfer results into the underlying 2.6 μm thick SiO_2 and/or directly into the Si-substrate by using RIE. We achieved excellent vertical side-walls free of passivation. The building of facets was observed to be on an acceptable scale.

Keywords: Chemically amplified resist (CAR); E-beam lithography (EBL); Reactive ion etching (RIE); T-top profiles; Deep pattern transfer; Vertical side-walls free of passivation

1. Introduction

Evolutionary developments in microelectronic manufacturing have shown the need to find simple technological methods to perform conformal deep structure transfer into the substrate with high anisotropy. The most critical processes are lithography and dry etching, whereby for both the resist used is the most critical factor. Conventional high-resolution resist materials in the direct e-beam lithographic (EBL) process show low sensitivity, poor dry etch durability in reactive ion etching (RIE), and swelling when developed by using organic solvents. It has been shown recently [1] that chemically amplified resists (CARs) based on polyhydroxystyrenesulfone can be used in EBL as well as in the deep-UV exposure mode; these resists can

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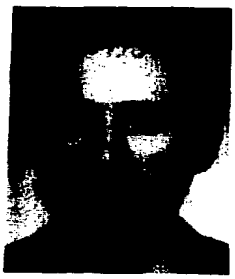
be developed in an aqueous alkaline solution. Also, preliminary studies [2] have indicated the suitability of these materials for masking during the dry etch processes typically employed in silicon IC manufacturing. In this work, this type of material is evaluated with regard to its possible application as a mask for micromachining.



Peter Hudek was born in Bratislava, Czechoslovakia. He received the Dipl-Ing. degree in 1977 and the Dr.-Ing. degree in 1987 from the Electrotechnical Faculty of the Technical University Bratislava. In 1977 he joined the Institute of Technical Cybernetics of the Slovak Academy of Sciences in Bratislava. He has worked in the field of developing e-beam lithography systems for multilayer direct electron-beam writing. Since 1982 he is in charge of developing experimental and theoretical models of sub micro- and nanometer processes for special devices. Currently he is a project leader at the Institute of Computer Systems and his research interests include non conventional lithographic and plasma processing techniques for microlithographic master-masks fabrication.

I.W. Rangelow was born in Lom, Bulgaria. He received the Dipl.-Ing degree in 1977 and the Dr. Sci.(Eng.) degree in 1981 from the Electron Technology Faculty of the Technical University Wroclaw, Poland in field of ion beam etching, microlithography, and ion beam sources. In 1992 he received a research fellowship and worked on electron, X-ray and ion beams at the University of Münster, Germany. In 1994 he was engaged in the field of X-ray lithography and X-ray masks at the Fraunhofer Institute für Mikrostrukturtechnik, Berlin, where he was involved in the research and development of dry etching processing for the developing of X-ray masks. In 1996 he joined the Institut für Technische Physik, Universität Kassel, Germany. Currently he is responsible for the group of microstructures technology. His research interests include e-beam, X-ray, ion-beam lithography, wet and dry etching for bulk-micro-machining, thin film, and resist technology. He is author of more than 70 publications, book chapters, and holds 3 patents.

Ivan Daraktchev graduated in 1972 as a Dipl. Engineer in Semiconductor Chemistry and Technology. From 1972 to 1982 he worked at the Institute of Microelectronics in Sofia, Bulgaria, where he fulfilled the functions of Processing Engineer and later Research Fellow and Department Manager. The projects he co-ordinated were first in the area of assembly and packaging (until 1975) and then dry processing and photolithography. From 1982 to 1984, he conducted research in ESAT Laboratory at KU Leuven, Belgium, on projects related to thin gate dielectric's characterisation. During this period he also obtained a MSc degree from the Dept. of Applied Sciences at the KU Leuven. In 1984, Ivan joined OCG Microelectronic Materials Inc. (at the time Munt Chemical), where he currently holds the position of Technical Director for Europe and supervises the R&D projects carried out at the laboratories of the Technical Service Center, dedicated to photolithography. He has authored or co-authored more than 30 scientific papers and 6 patents.

Ivan Kostić received his BS degree in Physics from Moscow State University, USSR, in 1980. He joined the Laboratory of Electron-Beam Lithography of the Institute of Technical Cybernetics at the Slovak Academy of Sciences, Bratislava, Czechoslovakia, where he was involved in the research and development of e-beam technology. Currently he continues his work in microlithography and microfabrication at the Institute of Computer Systems of the Slovak Academy of Sciences.

After more than 10 years' investigation of CARs (mainly using Novolak as base polymer) in connection with conventional photo-lithography deep-UV, X-ray, e-beam, and ion-beam lithography, there exists a lot of experience about how to use these resists, and we have learned about their performance and limitations. Although a good literature base exists about the UV applications of CAMP6 [3–6], there has been very little written about it in connection with EBL [1,3] and RIE [2] applications. In this work we would like to report on EBL and RIE experiments conducted on a new, non-Novolak-based CAR material, the positive working deep-UV resist CAMP6.

2. Experimental

2.1. EBL performance

E-beam exposure was applied by a 30 keV pattern generator (modified ZBA 10/1 made by Carl-Zeiss-Jena) onto CAMP6, a t-BOC-protected polyhydroxystyrenesulfone copolymer. Typically, 0.6–1.0 and 1.7 μm resist was spin-coated, which was then covered with BC-5, providing a protective coating of 65 nm thickness. The film thicknesses were measured using either a Talystep or a Dektak stylus profilometer. The process sequence for CAMP6 resist material is shown in Table 1.

After this processing we obtained our resist-relief structures. We investigated the characteristics using a special exposure test which is a very fine exposure wedge. The set of structures was exposed periodically with doses increased by a very small increment (25 nC/cm^2). By use of them we can measure the basic resist characteristics and the influence of the proximity effects as well. The resolution parameters from our experiments were determined and linewidths were measured by examining the gold-coated samples using a Hitachi S-4000 low-voltage high-resolution field-emission scanning electron microscope (FE-SEM). Contrary to Novolak-based CARs, varying the PB temperature (90–130°C) has no detectable effect on

Table 1

Wafer priming in air	HMDS/60 s
Resist spin coating	0.65 μm, 6000 rpm
	1.00 μm, 2379 rpm
	1.70 μm, 850 rpm
Pre-bake (PB) on hot plate (HP) in air	120°C, 60 s
Protective layer spin coating (BC5)	0.065 μm, 4000 rpm
PB on HP in air	120°C, 60 s
E-beam exposure	30 keV
Post-exposure bake (PEB) on HP in air, immediately after e-beam exposure	120°C ± 2°C, 60 s ± 5% (also 80–150°C, 60 s)
Development (immersion)	OPD-262 developer
	15, 30, 60, 120, 240, 360 s
Rinse	DI water, 20 s
Dry spinning in air	1000 rpm, 60 s
Hard bake (HB) on HP in air	120°C, 60 s

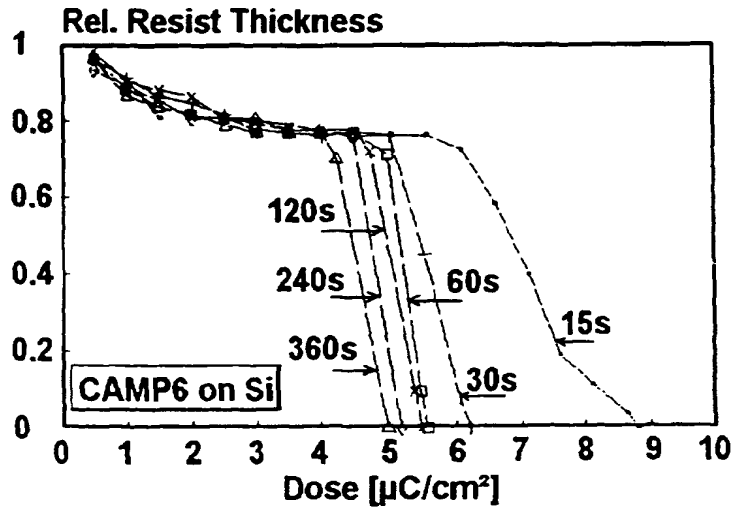


Fig. 1. Dissolution curves for 1 μm thick CAMP6 resist at various development times.

CAMP6 lithographic parameters (resolution, sensitivity, and contrast) because of the high T_g (glass transition temperature) of the CAMP6 comprised resin.

Various post-exposure bakes (PEB) were studied, and immersion development in OPD 262 (2.38 wt% TMAH in water) was applied at various development times. Typical dissolution curves for 1 μm thick CAMP6, obtained by varying the exposure doses in small increments are shown in Fig. 1. The effect of PEB temperature (80–150°C) on the critical exposure dose related to the relative resist sensitivity (clearing dose required for large areas) is depicted in Fig. 2.

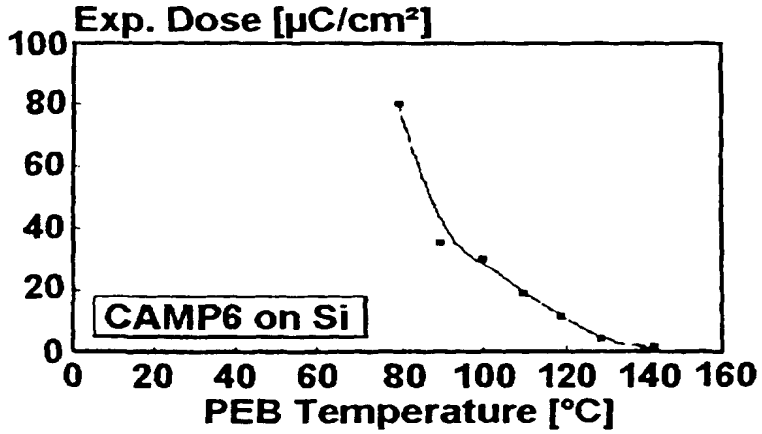


Fig. 2. The dependence of the resist sensitivity on the applied PEB temperature.

The PEB parameters, e.g. temperature (T_{PEB}), time (t_{PEB}) and the PEB delay (time delay between the exposure and PEB steps) are the most critical parameters in the CAMP6 handling process. PEB is primarily responsible for the dissolution selectivity in the development process. A PEB immediately after exposure is necessary to assure base solubility in the exposed areas [3]. For a good process reproducibility a reasonable degree of control is required over the used temperature (±2°C) and time (±5%). The relative resist sensitivity value is even smaller with increasing PEB delay. The exposed areas in the developer were insoluble with PEB delays in excess of 10 min or PEB temperatures below 70°C.

We observed a relatively large resist-film thickness loss of non-exposed areas after PEB and development (associated with the loss of CO_2 and isobutylene) for constant developer concentration (C_{dev}). From initial resist thicknesses of 1.7 μm, 1.0 μm and 0.65 μm the remaining thicknesses were 1.3 μm, 0.77 μm and 0.49 μm, respectively, which means an average loss of 23–25%.

The dissolution rate (R) of CARs is strongly affected by thermally driven catalytic reactions during the PEB. Therefore a classical semi-empirical dissolution rate model (1) for typical e-beam resists [7] does not give an accurate prediction of resist profiles without performing a large number of experiments.

$$R = \frac{R_0}{(1 + (E/E_0)^{\beta})^{\alpha}}, \tag{1}$$

where E is the energy deposition, R_0 the dissolution rate of unexposed resist, obtainable directly from physical measurements, and E_0, α, and β are fitted from non-linear regression.

2.2. Application to submicro- and nanometer structure patterning

The smaller the minimum feature sizes, the greater is the demand to quantify and optimise the lithographic process steps to obtain resist patterns with details within the required tolerance. The experimental characteristics of resist-relief structures obtained for a variety of processing conditions and exposure parameters for isolated lines and proximity-affected structures helped to find a way to optimise the lithographic process by using the calculated electron energy deposition (E) in the irradiated resist volume. However, the simulation using the dissolution rate as a function of absorbed energy cannot be used to predict the optimal PEB and development conditions, due to the lack of an exact mechanistic model of this resist dissolution mechanism. The capability of the traditional $R = f(E)$ (1) must be extended for CARs to $R = f(t_{PEB}, T_{PEB}, C_{dev}, \ldots, E)$. The models used for the Novolak-based positive CAR resist described in [8,9] are not satisfactory for CAMP6 because of some abnormal resist behaviour which will be discussed here. Therefore, up to now, we can use only the results obtained from the dose calibration to choose an optimised exposure and resist-handling process.

Pre-development delays up to 1 hour have no effect on the CAMP6 lithographic properties.

The development is not very critical for all process parameters. Assuming a correct exposure, a well-shaped structure in the exposed areas in the resist appears after about 15–20 s. However, the development mechanism shows interesting effects on the resulting

resist-relief structures, mainly in thicker (1.7 μm) CAMP6. Fig. 3 shows the profile evolution of a 0.5 μm exposed line vs. exposure doses. In the case of underexposure and slightly below the clearing dose, the profile is atypical and not easily explainable. The shaped e-beam used in this case is 0.5 μm in width and the line profile obtained consists of two levels: (i) a top level and (ii) a small trench at the bottom, in which the profile is V-shaped (Fig. 4.). For profiles with vertical walls it is necessary to expose with 22 $\mu C/cm^2$, which is 4 times the dose required for a 10 μm linewidth (intra-proximity effect). This indicates a very steep dose correction curve for 1.7 μm thick CAMP6 compared to typical PMMA or Novolak-based positive CARs [10]. This non-conventional resist behaviour is typical mainly close to the critical absorbed energy density necessary to completely clear the resist. Small decreases in the exposure energy from the clearing dose causes the development of the exposed volume to be V-shaped. The development mechanism shows extreme contrast where portions of this region are clear and others retains a complete resist thickness. This effect can be partially explained by the fact that the rate of deprotection is a strong function of dose, but dramatically decreases when about 90% of t-BOC deprotection is achieved [3]. Thus, it seems to have a step-function-like dependence on t-BOC concentration, and only a small increase in t-BOC concentration (5%) makes the resist base insoluble. Also it is not yet clear how the formation of microcracks in corners of the resist patterns in this relatively thick resist film can be explained.

Furthermore, we have investigated the resist profile shape dependence on the development

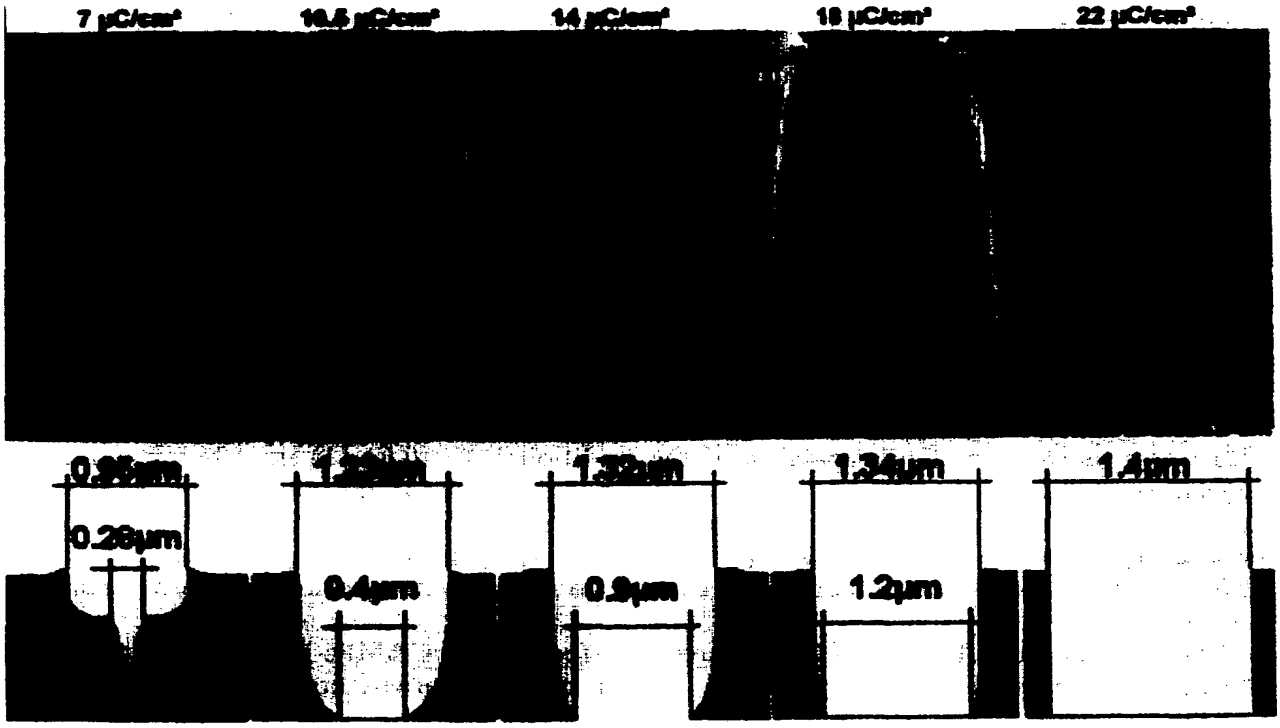


Fig. 3. Single-line resist-profile evolution at various exposure doses in 1.7 μm thick CAMP6.

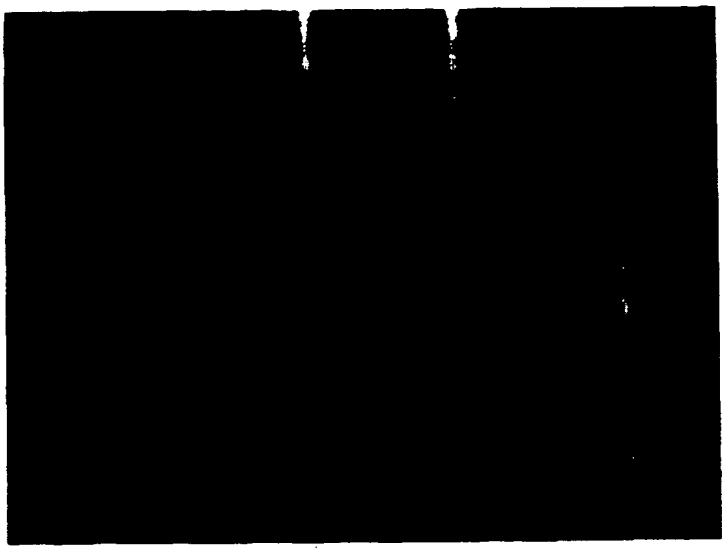


Fig. 4. V-shaped resist profile of an under-exposed line in 1.7 μm thick CAMP6.

time. Details of a doughnut-like pattern are shown in Fig. 5. (1.0 μm outer diameter, 0.4 μm inner diameter) exposed into 1.7 μm thick CAMP6 developed for 60 s (a) and for 240 s (b). The relative exposure intensities necessary to create the critical amount of radiation-chemical changes in the polymer are nearly the same for both cases. This indicates the dimensional lateral measurements of both patterns and the structural configuration of the inner pillars for 60 s and 240 s development conditions at 16 $\mu C/cm^2$ and 6.5 $\mu C/cm^2$ exposure doses.

(a) (b)

Fig. 5. Doughnut-like exposed resist patterns developed for: (a) 60 s at 16.0 $\mu C/cm^2$, (b) 240 s at 6.5 $\mu C/cm^2$.

respectively. As Fig. 5.b shows, a low exposure dose combined with an adequate longer development time gives a better defined and more vertical resist profile than do higher doses and shorter development times. Thus, the extremely low dose requirement is advantageous from the standpoint of wafer throughput. However, this causes problems in maintaining sufficient linewidth control at smaller critical dimensions (CDs) in the exposure-dose optimisation process. This is due to the fact that the exposure-field uniformity in these cases is influenced by effects such as shot noise, which causes edge-noise and linewidth variation.

The next subsection discusses the problem of line arrays. The minimal obtained line/space ratio (L/S) is used in lithography as a limiting resolution parameter for a given resist system. The resolution of CAMP6 material reported in [4] as having been obtained was 0.25 μm in 0.3 μm resist film and in [1] 0.2 μm of L/S in 0.65 μm thick resist, respectively. In the dimension range up to 0.5 μm we can obtain an array of parallel lines with good CD control and vertical side-walls for CAMP6 film thicknesses up to 1.5 μm under optimised exposure conditions. For patterning of structures with features below 0.5 μm the observed structures show the developing of so-called "T-top" line profiles, which are also typical for other CARs [8,11]. Fig. 6 depicts obtained resist lines, 50–80 nm in width in the bottom part, exposed into 1.7 μm CAMP6. The 60 nm thick T-top part of the resist line could be due to the effect of surface dissolution retardation of this top resist layer.

The insolubility seems to be a surface phenomenon, since the areas under this top layer are clear and homogenous. This observed surface phenomenon can be associated with the airborne contamination of the resist during the time of resist spin-coating, PB and the protective-layer spin-coating. In order to moderate this resist-surface retardation effect (reaction of the photoacid with air contaminants), we kept this delay as small as possible (max. 2 min) in our experiments.

Fig. 6b shows that the T-top formation is a high-contrast process with very sharp contours of the contaminated (photoacid depletion) zone. Under this "skin" there is a homogeneous bottom non-contaminated volume of resist, where the structures are developed with high

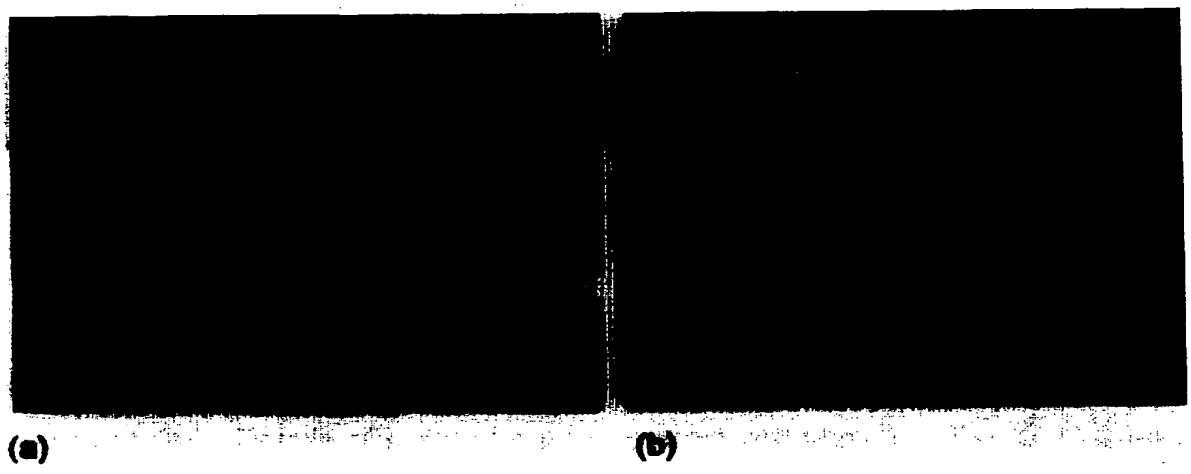


Fig. 6. High-aspect-ratio (about 20) nanometer T-top profiles in 1.3 μm thick CAMP6.

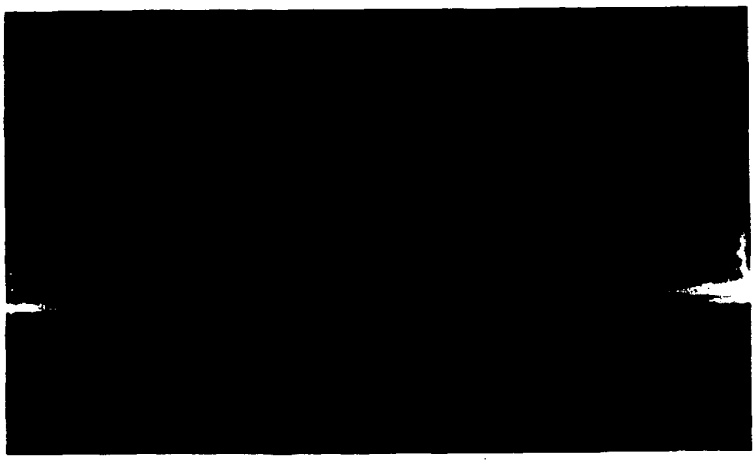


Fig. 7. "Bridging" of densely exposed patterns due to the resist-surface dissolution retardation effect.

aspect ratio (more than 20) in 1.3 μm thick resist film. It is clear that such changes in the dissolution properties of the resist strongly affect the resolution possibilities. This shrinks the process latitude and causes extensive variation in pattern dimensions on submicro- and nanometer scale. One pattern-distortion effect is the "filling" or "bridging" of the surface of densely exposed structures which gives a tunnel-like appearance as shown in Fig. 7.

Fig. 8 shows an over-exposed dot array, where the bottom non-contaminated resist is dissolved in the developer and the non-solvable contaminated layer has collapsed.

All of the effects cited up to here have a severe dependence on the exposure optimisation and correction of the proximity effects in CAMP6, mainly in the sub-halfmicron region. At first glance, one can show other effects as in typical positive resists. Therefore, with the standard algorithms in existing simulation models of lithographic processes, one cannot simulate these effects in CAMP6. One example of such an effect which is impossible to

Fig. 8. Array of over-exposed dots in resist with collapsed topcontaminations layer.

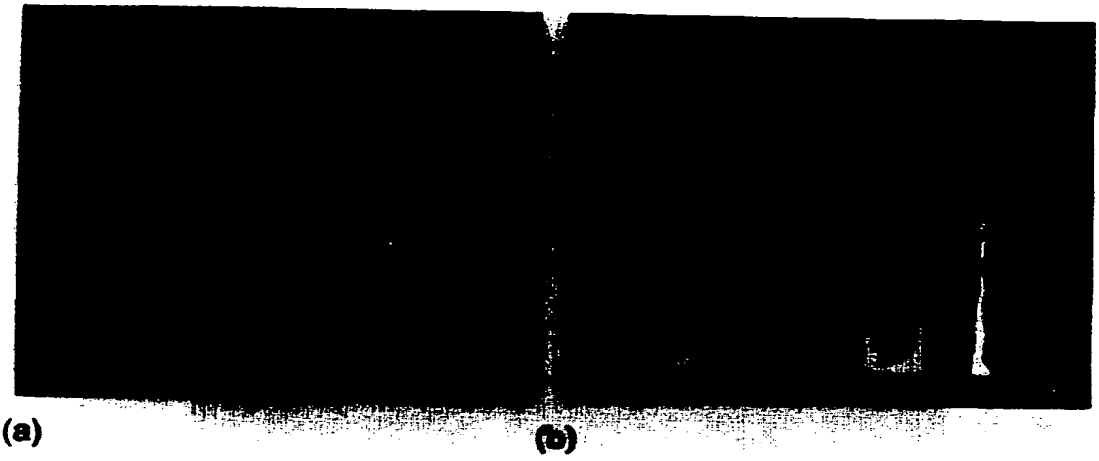


Fig. 9. Inter-proximity effect of parallel lines in (a) 0.5 μm and (b) 1.7 μm thick CAMP6 resist exposed with (a) 10.5 μC/cm² and (b) 52.5 μC cm² dose.

simulate is shown in Fig. 9, where three parallel lines 0.1 μm in width are exposed sequentially from left to right into 0.5 μm and 1.7 μm thick resist. Symmetrically shaped proximity "explosion" for thicker resist layer seems to have occurred in the middle of this array (Fig. 9.b).

2.3. *Application to MST pattern fabrication*

Because we are interested and engaged in the dry etching of deep micromechanical structures, thicker resist films with vertical lithographic resist profile are required. In the area of micro-system technology (MST) the resolution criterion is obviously not under a half-micron and also the patterned structures are not so densely packed together. Therefore, the mentioned pattern-deformation problems seem here to be less severe for larger MST structures. SEM micrographs of our experiments in the next chapter also reveal that the obtained CAMP6-relief structures are well suited for deep single resist-layer structure transfer by using dry etching. The only important factor is in the relatively wide process window, where the most critical step is control of the PEB delay within a few seconds. The correction of the e-beam exposure process is also necessary because of a very sharp intra-proximity dose dependence. We optimised the exposure by using the dose-correction curve for structure details above 0.5 μm. For smaller and closely spaced (inter-proximity affected) structures the exposure requires an additional geometrical correction. Our e-beam pattern generator equipped with a very fine individual shape-by-shape dynamically programmable dosage control enabled us to create CAMP6 masking structures with nearly vertical side-walls. This is a necessary condition for a subsequent successful pattern transfer with vertical and controlled slope profiles into the substrate.

2.4. RIE

Poly(hydroxystyrene), which is the base resin of CAMP6, has a high T_g (165°C). In the sulfone copolymer this results in thermally stable resist images with a high resistivity to RIE. The high etch selectivity and the good resolution of high-aspect-ratio patterns with vertical side-walls make CAMP6 well suited for single-resist layer deep etching of micromechanical parts and also for fine features.

RIE on 2.6 μm thick thermally grown SiO_2 was performed in the PLASMALAB reactor with a CHF_3/Ar gas mixture at a pressure of 2.5 mTorr and at 1.3 W/cm^2 power density ranges. Under these plasma etching conditions, features 0.5 μm and smaller were transferred successfully deeply into SiO_2. The average selectivity of CAMP6 to SiO_2 in CHF_3/Ar is in the range from 8 to 11, depending on the etching parameters. The etching rate of CAMP6 varies with etching time. The initial erosion rate of the resist is high until about 40% of the thickness is lost (probably due to initial rapid loss of t-BOC groups because of an exposure of the top of the resist to the UV and/or electrons of the plasma emission). Then the resist etch rate becomes substantially lower (about 2 nm/min).

Typical results of fine-line submicrometer and micromechanical resist/SiO_2 structures obtained after applying our RIE process to the dose/geometry exposure corrected resist mask are shown in Figs. 10 and 11.

Differences were noticed in the formation of side-wall polymers using CAMP6 in SF_6/Ar plasma in single-layer CAMP6/silicon RIE processes compared to previously used Novolak-based CARs. Additional experiments are needed in order to explain this. The etch selectivity of silicon to CAMP6 with vertical side-walls obtained was between 2.4 to 2.7 at a pressure of 5.5 mTorr and at about 130 mW/cm^2 power density.

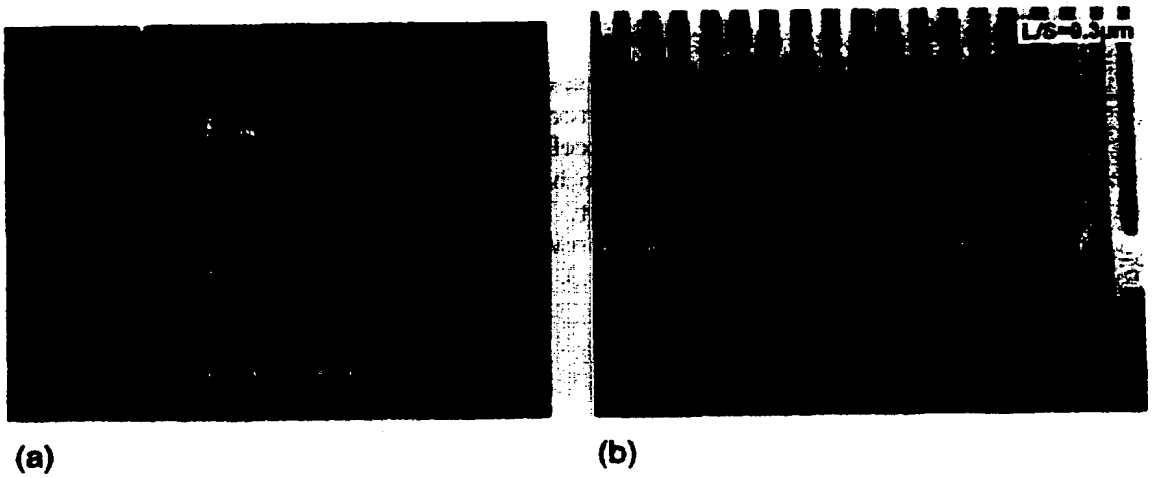


Fig. 10. Fine-line structures etched into 2.6 μm SiO_2 layer. (a) Combined line/area structure with 0.5 μm minimum L/S. (b) Line array with 0.3 μm L/S.

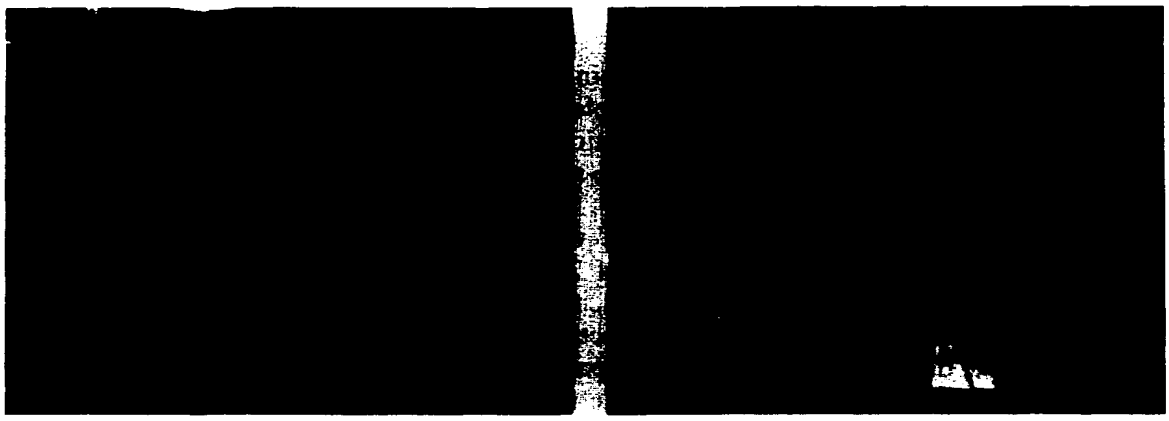


Fig. 11. Patterns etched into 2.6 μm thick SiO_2.

Also, Cl- and Br-containing deep-RIE was performed with single-layer CAMP6. The results from these processes are yet not completed and will be presented in the near future.

Conclusion

The chemically amplified positive resist system CAMP6 under EBL and RIE exhibits high contrast, good resolution, very good thermal stability and a good process window. The PEB delay appears to be the most critical parameter in the whole handling process.

The e-beam exposure requires an exact dosage optimisation and the inter-proximity affected patterns in the submicron region require an additional geometrical correction. Due to the lack of a mechanistic resist-dissolution model for this polymer we can not yet simulate the EBL process without the use of a time-consuming experimental dose-calibration method. By using this method and the shape-by-shape dose correction we have obtained resist-gap structures with about 50–80 nm resolution, and an excellent aspect ratio of about 20 and vertical side-walls. The CAMP6 resist is proven here to have a good stability in the SF_6/Ar plasma in commercially available plasma etch equipment. The deep etching into a 2.6 μm thick SiO_2 layer through 0.6–1.7 μm thick CAMP6 showed a very good process compatibility for patterning micromechanical structures up to 0.3 μm structure details.

Acknowledgements

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